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THEORETICAL AND EXPERIMENTAL STUDY OF THE ABSORPTION RATE OF H_2S IN $CUSO_4$ SOLUTIONS
The Effect of Enhancement of Mass Transfer by a Precipitation Reaction

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Abstract: In this paper the desulphurization of gas streams using aqueous copper sulphate ($CuSO_4$) solutions as washing liquor is studied theoretically and experimentally. The desulphurization is accomplished by a precipitation reaction that occurs when sulphide ions and metal ions are brought into contact with each other.

Absorption experiments of H_2S in aqueous $CuSO_4$ solutions were carried out in a Mechanically Agitated Gas Liquid Reactor. The experiments were conducted at a temperature of 293 K and $CuSO_4$ concentrations between 0.01 and 0.1 M. These experiments showed that the process efficiently removes H_2S. Furthermore, the experiments indicate that the absorption of H_2S in a $CuSO_4$ solution may typically be considered a mass transfer limited process at, for this type of industrial process, relevant conditions.

The extended model developed by Al-Tarazi *et al.* (2004) has been used to predict the rate of H_2S absorption. This model describes the absorption and accompanying precipitation process in terms of, among others, elementary reaction steps, particle nucleation and growth. The results from this extended model and results obtained with a much simpler model, regarding the absorption of H_2S in $CuSO_4$ containing aqueous solutions as absorption of a gas accompanied by an instantaneous irreversible reaction were compared with experimental results. From this comparison it appeared that the absorption rate of H_2S in a $CuSO_4$ solution can, under certain conditions, be considered as a mass transfer rate controlled process. Under a much wider range of conditions the error that is made by assuming that the absorption process is a mass transfer controlled process, is still within engineering accuracy. Application of the simple model allows for a considerable reduction of the theoretical effort needed for the design of a gas–liquid contacting device, thereby still assuring that the desired gas specification can be met under a wide range of operating conditions.

A comparison of the experimental results and the simulated results showed that the extended model gives an under prediction of the H_2S absorption rate for the experimental conditions applied.

Keywords: desulphurization; metal sulphide; precipitation; reaction; kinetics; gas treating; absorption.

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INTRODUCTION

Gas–liquid processes are commonly employed in the chemical industry, for example when reacting gaseous and liquid reactants. In the case of removal of H_2S from a gas stream, the scrubbing solution may contain dissolved basic reagents (e.g., alkanolamines or NaOH), oxidizing chemicals (e.g., Fe^{3+} ligands) or components forming solids upon the reaction with S^{2-} (like most Me^{2+} ions). For a more complete overview of the existing technologies we would like to refer to the textbook by Kohl and Nielsen (1997). When the absorbed gaseous component reacts in the liquid, it is possible that the rate of absorption of the gaseous component is enhanced by the chemical reaction. Understanding how the reaction (rate) influences the gas absorption rate is therefore a vital prerequisite for a reliable design of a contactor.

For simple irreversible reactions this effect can readily be estimated using analytical or approximate solutions of various mass

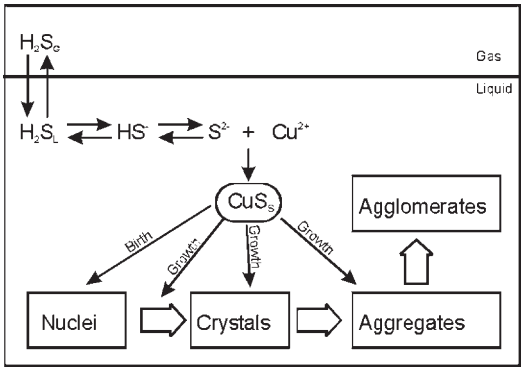

Figure 1. Schematic overview of the process steps during H2S absorption in an aqueous solution containing copper sulphate.

transfer models. These analytical solutions can for example be found in the textbook of Westerterp *et al.* (1984). For other cases (e.g., non-instantaneous complex or non-instantaneous equilibrium reactions) the effect of the reaction on the gas absorption rate cannot be determined analytically, making a numerical approach necessary. For the case of H_2S absorption in, and reaction with, a metal sulphate containing solution, the rate at which H_2S absorbs in the solution is the result of a number of process steps involving absorption and reaction. All process steps (see Figure 1) need to be taken into account to yield an accurate description of the H_2S absorption process.

Unfortunately, not much is known about the exact reaction rate of S^{2-} with the metal ions, although some precipitation models are available in literature. The reaction rate at which S^{2-} and metal ions react to form solid metal sulfide is determined by two processes: firstly, the formation of new metal sulphide nuclei and, secondly, the growth of existing precipitates. These precipitation models state that the rate of formation of new precipitate particles is a highly non–linear function of the concentration of the reacting components (Nielsen, 1964; Söhnel and Garside, 1992). Furthermore, the rate of growth of existing particles is to be the result of a number of process steps (like diffusion of reacting components to the precipitate surface and the rate at which the ions are incorporated in the crystal), all of which can be rate-limiting.

Clearly an accurate model incorporating all absorption and reaction steps is required to describe the rate of absorption of H_2S in a metal salt solution. Such a model has been developed by Al-Tarazi *et al.* (2004). This extensive model was developed as a tool for the design of contactors for the removal of heavy metal salts from a liquid stream using H_2S, but can theoretically also be used as a tool for the design of contactors for the removal of H_2S from a gas stream using metal salt solutions. Parallel to this extensive model, experimental results (e.g., ter Maat *et al.*, 2005) seem to indicate that, for many operating conditions, the absorption of H_2S into a $CuSO_4$ solution can also be described with a simple model that considers the absorption of H_2S in a $CuSO_4$ solution to be a process of mass transfer accompanied by an instantaneous irreversible reaction, or even as gas phase mass transfer limited absorption process. This simplified model can be regarded as an asymptotic case of the extensive model of Al-Tarazi *et al.* (2004). In this contribution the theoretical results of this simplified approach will be compared with the theoretical results of the rigorous model of Al-Tarazi *et al.* (2004), and the applicability of this simplified approach will be discussed. Apart from this, an extensive experimental study on the absorption of H_2S in various copper sulfate solutions has been performed, and these results will be discussed and also compared to the results of the theoretical predictions.

LITERATURE

The use of H_2S for the (selective) precipitation of valuable metal compounds from leaching solutions has been known to the ore refining industry for a long time (for a review see Kroschwitz and Howe-Grant, 1991). Thus far, only limited fundamental research on the phenomenon of absorption of H_2S in a solution, accompanied by a precipitation reaction of a highly insoluble metal sulphide, has been performed. The work of Mishra and Kapoor (1978) can be regarded as a pioneering attempt to couple the mass transfer theory of absorption of a gas in a reactive liquid and the theory of precipitation dynamics. They investigated the precipitation of cadmium(II) sulphide from a cadmium(II) chloride solution in a bubble column reactor. The absorption of pure H_2S in a diluted cadmium chloride solution could, according to their own conclusions, be described by assuming that the absorption of H_2S into the solution was accompanied by an instantaneous irreversible reaction between H_2S and the metal ion. The mass transfer model used in their study was based on the Higbie penetration model (Higbie, 1935). It must be noted however that the cadmium chloride concentration applied was so low, that the influence of the reaction of the absorption rate was rather small, and therefore that the reliability of their conclusions might be debatable.

The absorption of H_2S into a diluted copper sulphate solution was investigated by Oktaybas *et al.* (1994), who used an experimental setup identical to the one used by Mishra and Kapoor (1978). Oktaybas *et al.* (1994) also used the Higbie penetration model and the assumption of an irreversible instantaneous reaction between H_2S and Cu^{2+} to explain the results. Although the agreement between theory and experiment was good for pH values larger than 2, their model did not explain the observed dependency of the absorption rate on the pH, observed at pH values below 2. Oktaybas *et al.* (1994) ascribed the decrease of the absorption rate with decreasing pH to the shift in the $H_2S/HS^-/S^{2-}$ equilibria and the resulting lower S^{2-} concentration.

Broekhuis *et al.* (1992) investigated the removal of dilute H_2S from a gas stream using copper and zinc sulphate solutions in a stirred cell reactor. Here, the rate of absorption of H_2S in a copper sulphate solution was found to be gas phase mass transfer limited, while the absorption rate of H_2S into a zinc sulphate solution was found to be a function of the amount of unconverted zinc sulphate. They did not attempt to present a fundamental description of the simultaneous absorption and precipitation of H_2S in metal sulphate solutions. ter Maat *et al.* (2005) investigated the removal of dilute H_2S from a gas stream using copper, zinc and iron sulphate solutions in a bubble column reactor. The $CuSO_4$ solution was shown to be the most suitable solution for H_2S removal. The laboratory experiments indicated that the absorption of H_2S in a $CuSO_4$ solution, at the experimental conditions tested, is a gas phase mass transfer limited process. In the same study the applicability of a $CuSO_4$ solution

for the removal of H_2S from a biogas stream was successfully demonstrated on a pilot plant scale.

Additionally, the use of metal salt solutions for desulphurization has been mentioned in open literature in articles by Manning (1979) and Brown and Dyer (1980), and in the patents of Spevack (1980) and Harvey (1980), but no model description of the absorption of H_2S into a metal salt solution, accompanied by a precipitation reaction, was presented. Such a more fundamental model, describing the absorption of H_2S into an aqueous solution of (a mixture of) metal salts, accompanied by a precipitation reaction, was developed by Al-Tarazi *et al.* (2004). This mass transfer model, which will also be used in this study, also takes specific precipitation related phenomena, such as the nucleation of new particles and particle growth, into account.

THEORY

Reaction Scheme

Upon the absorption of H_2S into an aqueous bivalent metal sulphate solution the following reactions will occur. After H_2S is dissolved in water [equation (1)] it dissociates in two steps according to equations (2) and (3):

$$H_2S(G) \longleftrightarrow H_2S(L) \tag{1}$$

$$H_2S + H_2O \underset{k_{1,2}}{\overset{k_{1,1}}{\longleftrightarrow}} HS + H_3O^+ \tag{2}$$

$$HS^- + H_2O \underset{k_{2,2}}{\overset{k_{2,1}}{\longleftrightarrow}} S^{2-} + H_3O^+ \tag{3}$$

When sufficient thermodynamic driving force (i.e., at a supersaturation ratio larger than 1) is present the subsequent precipitation reaction between the sulphide ion formed during the second dissociation step, and the metal ions can occur:

$$Me^{2+} + S^{2-} \xrightarrow{k_3} MeS \downarrow \tag{4}$$

The supersaturation ratio is defined as[1]

$$S = \frac{[Me^{2+}][S^{2-}]}{K_{SP}} \tag{5}$$

Other reactions that occur are the water equilibrium [equation (6)], and the dissociation reaction of the bisulfate ion [equation (7)]:

$$H_3O^+ + OH^- \underset{k_{5,2}}{\overset{k_{5,1}}{\longleftrightarrow}} 2H_2O \tag{6}$$

$$HSO_4^- + H_2O \underset{k_{6,2}}{\overset{k_{6,1}}{\longleftrightarrow}} H_3O^+ + SO_4^{2-} \tag{7}$$

The equilibrium constants of equations (2)–(7) are presented in Table 1.

Table 1. Equilibrium constants.

Reaction	Equilibrium constant	Numerical value pK	Source
2	$K_{a1,H_2S} = \frac{[HS^-][H_3O^+]}{[H_2S]}$	6.97	Horvath (1985)
3	$K_{a2,H_2S} = \frac{[S^{2-}][H_3O^+]}{[HS^-]}$	12.9	Horvath (1985)
4	$K_{SP} = [Me^{2+}][S^{2-}]$	23.7 for ZnS 39.2 for CuS	Dean (1992)
6	$K_w = [H_3O^+][OH^-]$	14	Horvath (1985)
7	$K_{a2,H_2SO_4} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$	2.0	Horvath (1985)

MASS TRANSFER MODELS

Extended Model Description

Al-Tarazi *et al.* (2004) have developed a model that describes mass transfer accompanied by a precipitation reaction (see Figure 1 for a schematic overview of the steps incorporated in the model). The model was specifically developed for the case of the precipitation of metal sulphides in an aqueous solution containing heavy metal ions (more specifically Cu^{2+} and Zn^{2+}) that is continuously contacted with a H_2S containing gas. This model aims to predict the effect of operation, process conditions and reactor layout on the rate of H_2S absorption, precipitation and particle size distribution. First, the model of Al-Tarazi, which has been adopted here in unchanged form, will shortly be discussed.

In Al-Tarazi's model, mass transport in the gas phase is modelled using the film model, and at the gas–liquid interface local equilibrium is assumed. The physical equilibrium solubility of the gas in the solvent can be estimated from literature data (Horvath, 1985). The mass transfer zone is modelled according to Higbie's penetration model (Higbie, 1935), and mass balances for all species have been set up incorporating equations (2)–(7). As a driving force not only the concentration gradient has been used, but the electrostatic potential gradient has also been taken into account. The concentration profile of the individual species in the mass transfer layer can be calculated as a function of contact time using

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - z_i D_i \frac{F}{RT} \frac{\partial(\phi C_i)}{\partial x} - r_i \tag{8}$$

With the exception of the rate of precipitation, all reaction rate equations are (the summation of) first order reactions. A separate mass balance for CuS has to be used since the rate of crystal growth and nucleation are separate functions of the supersaturation ratio and for these population balances have been used (for details see Al-Tarazi *et al.*, 2004).

The electrostatic potential needed in equation (8) can be calculated by use of the Nernst–Einstein equation (Newman, 1973) (for this type of systems typically resulting in dynamic electroneutrality).

$$\phi(x,t) = \frac{RT}{F} \frac{\sum_{i=1}^{NC} z_i D_i (\partial C_i / \partial x)}{\sum_{i=1}^{NC} z_i^2 D_i C_i} \tag{9}$$

The linear growth rate of particles is described by (Al Tarazi *et al.*, 2004):

$$G = k_g \left[\sqrt{\frac{C_{Cu^{2+}} C_{S^{2-}}}{\sqrt{K_{SP}}}} - 1 \right]^g \tag{10}$$

[1]Note that no allowance has been made for non-ideal behaviour in the equilibrium model.

The molar growth rate of particles is given by (Al Tarazi *et al.*, 2004):

$$G' = \sum_{i=1}^{\infty} \{\beta\rho n(z,L_i^2) G L_i^2 (L_i - L_{i-1})\} \quad (11)$$

And the molar rate of birth of new particles B' is expressed by (Al Tarazi *et al.*, 2004):

$$B' = \alpha\rho L_0^3 * k_n \left[\frac{\sqrt{C_{Cu^{2+}} C_{S^{2-}}}}{\sqrt{K_{SP}}} - 1 \right]^n \quad (12)$$

The particle size distribution of the formed metal sulphide particles has been calculated using the population balance as proposed by Randolph and Larson (1988). Further details of the model description, the applied boundary conditions and relations used to describe the population balances can be found in Al-Tarazi (2004). For the relation between the various chemical reactions the reader is referred to Figure 1.

The nucleation and precipitation growth parameters as needed in equations (10)–(12); (α.L_o. k_g, g, k_n and n) have been determined by Al Tarazi *et al.* (2004) by doing laminar jet experiments of gaseous H_2S in $CuSO_4$ solutions (Al-Tarazi *et al.*, 2004). Using these data, the model can now be used for the prediction of the H_2S absorption rate under various process conditions.

Simplified Model Description

It is likely that for a process in which highly insoluble precipitates (as is the case for copper sulphide) are formed, the precipitation (nucleation) may be considered to be fast or even instantaneous with respect to mass transfer (Söhnel and Garsides1992; Nielsen, 1964). In that case, it is possible to derive a simple set of equations that describe the rate of absorption.[2] For gas absorption accompanied by an instantaneous irreversible reaction the rate the absorption is determined by the mass transfer on both sides of the gas–liquid interface. Two cases can be distinguished: (1) a gas and liquid phase mass transfer limited regime and (2) a gas phase mass transfer limited regime.

Case 1: Gas and Liquid Phase Mass Transfer Limited Regime

In case of an instantaneous irreversible reaction, components A (H_2S) and B (Cu^{2+}) cannot exist simultaneously at the same location in the solution. In this case the overall mass transfer (volumetric transfer rate) can be described by equation (13).

$$J_{H_2S} a = \frac{C_{H_2S,G} E^*_{H_2S}}{(1/m k_{L,H_2S} a) + (1/k_{G,H_2S} a)} \quad (13)$$

For the film model the enhancement factor of the instantaneous irreversible reaction (for the overall mass transfer) $E_{H2S,\infty}{}^*$ is then defined as given in equation (14) [definition of equation (14) according to film model].

$$E^*_{H_2S,\infty} = \left(1 + \frac{D_{Cu} C_{Cu,L}}{D_{H_2S} m C_{H_2S,G}}\right) \quad (14)$$

[2] H_2S, HS^- and S^{2-} are assumed to be at equilibrium with each other at all time since these equilibrium reactions involve a proton transfer to or from a water molecule only.

Case 2: Gas Phase Mass Transfer Limited Regime

If the mass transfer rate of Cu^{2+}-ions from the liquid bulk to the interface is high compared to the mass transfer rate of H_2S from the gas bulk to the interface, the gas side mass transfer resistance entirely determines the rate of absorption. The gas side limited mass transfer of H_2S is expressed by

$$J_{H_2S} a = k_{G,\,H_2S} a C_{H_2S} \quad (15)$$

In case the simplification is allowed, the minimum of these two boundary cases 1 and 2 defines the overall mass transfer rate in the absorption process. In this study, it will be investigated to which degree, and under which conditions, this simplification is allowed. A comparison of the absorption rate as predicted with the model and the extended model of Al-Tarazi will be made (Al-Tarazi *et al.*, 2004, a short description is given in the paragraph 'Comparison with extended model'). Furthermore, H_2S absorption experiments will be carried out to verify the validity of both the extended model described by Al-Tarazi and the simplified model that assumes an instantaneous irreversible reaction

EXPERIMENTAL SETUP

The experiments were performed in a Mechanically Agitated Gas-Liquid Reactor (MAGLR) (see Figure 2). The experimental setup consisted of a gas mixing section, in which the desired gas flow could be composed, a reactor section, and a gas analysis section. The MAGLR was operated batch wise with respect to the liquid phase and continuously with respect to the gas phase.

The glass double walled reactor, internal diameter 8.25 cm, volume 1065 cm^3, was operated batch wise with respect to the liquid phase and continuously with respect to the gas phase.

The liquid could be intensely stirred with a six bladed Ruston turbine, diameter 45 mm, height 11 mm, located 42 mm from the bottom of the reactor. The gas phase was mixed with a two-bladed stirrer with a diameter of 72 mm. Both stirrers were mounted on a single axis with a diameter of 10 mm. The speed of the stirrer could be varied between 0 and 2000 rpm. The reactor was equipped with four baffles with a height of 104 mm and a width of 8 mm. Gas was sparged into the liquid with a diffusor placed about halfway the turbine stirrer and the bottom of the reactor. The diameter of the diffusor was 25 mm. The diffusor had five holes in a rectangular pitch with a diameter of 1 mm.

Isothermal operation was ensured by pumping water with a constant temperature from a thermostatic bath (Tamson T 1000) through the annular space of the double walled reactor. The temperature of the reactor contents was measured using a K-type thermocouple (accuracy 1 K). The pressure in the reactor was determined with a Druck PDCR 910 pressure transducer (accuracy 1 mbar).

In the gas mixing section a feed gas mixture with the desired flow rate and composition was prepared from pure gases using Brooks 5150 thermal mass flow controllers. The gas leaving the reactor was led through a caustic scrubber, before discharge to the atmosphere. A Tescom series 1700 back pressure regulator was used to regulate the reactor operating pressure.

For H_2S absorption experiments the gas–liquid reactor was filled with the desired solution (metal sulphate or

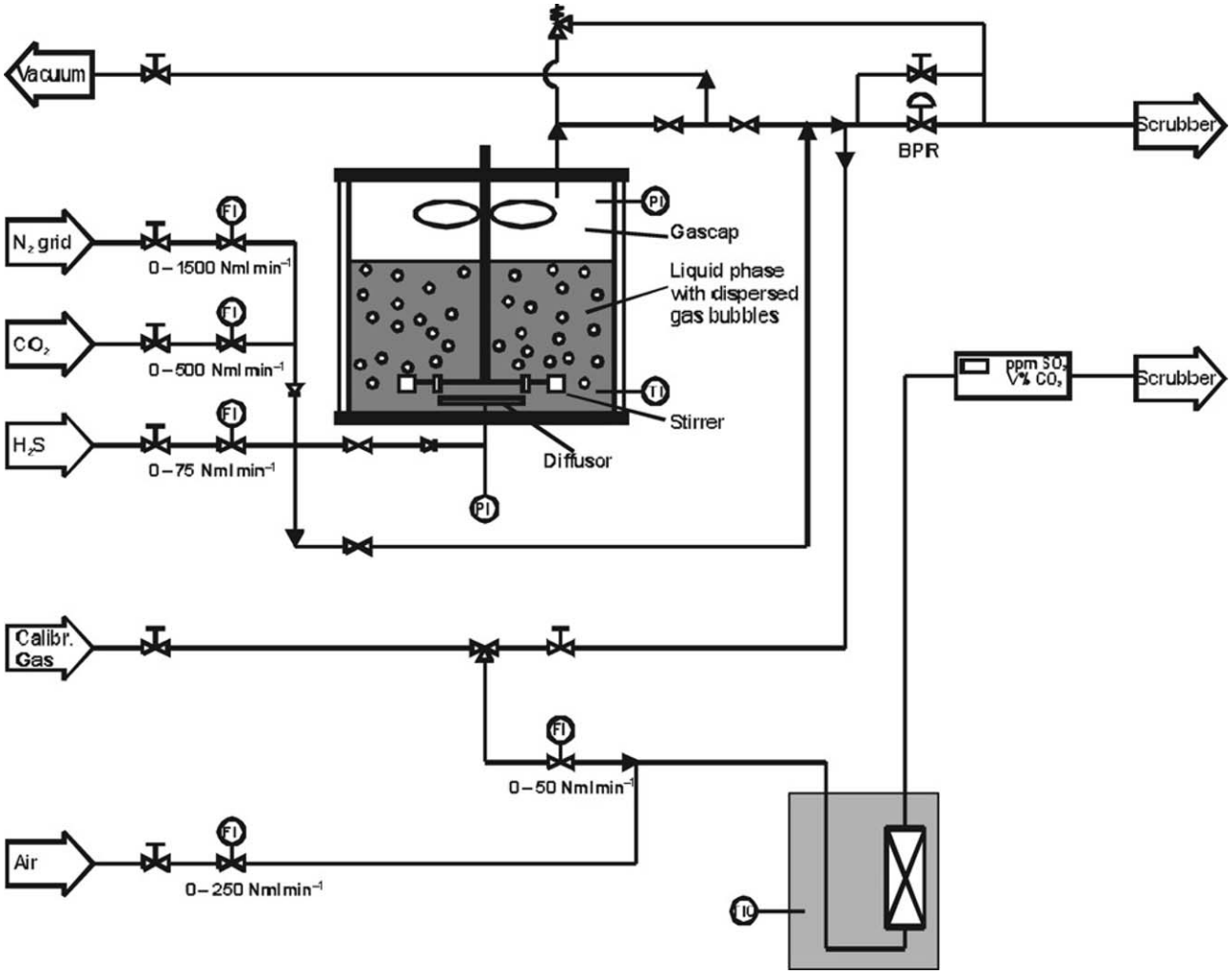

Figure 2. Schematic representation of the experimental setup.

sodium hydroxide). To avoid interference from gasses that might have absorbed from the atmosphere (e.g., N_2 or CO_2), the reactor content was subsequently degassed by evacuation. The temperature of the metal sulfate solution in the reactor was maintained at 293 K, after which, at $t = 0$, a gas stream with the desired composition was fed into the reactor at a flowrate of 5.0 Nml s^{-1}.[3] The pressure in the reactor was kept at 120 kPa. A small gas sample stream from the reactor effluent was diluted with air, and the H_2S in that stream was converted to SO_2 at 350 °C over stainless steel wool as catalyst. The resulting SO_2 concentration in the sample stream was determined using a MAIHAK MULTOR 610 multicomponent IR analyser, which simultaneously was able to determine the CO_2 concentration if any CO_2 was present in the gas (for details see also Ter Maat *et al.*, 2005; the accuracy of this method is 2.5%).

The volumetric mass transfer coefficient of the MAGLR was determined from CO_2 absorption experiments in pure water or metal sulphate solutions. These experiments were performed either by adding CO_2 to a stream of pure N_2 (to determine the physical characteristics of the setup), or to a mixture of N_2 and H_2S (to determine the $k_{OV}a$ during an actual H_2S absorption experiment.

$CuSO_4$ and NaOH (analytical grade) were obtained from Across Chimica, N_2 and CO_2 (purity of at least 99.9%) and H_2S (purity of 99.0%) were obtained from Hoek Loos. The calibration gas was prepared by Scott Specialty Gasses, and had a composition of 1.0 V% $H_2S \pm 0.05$%. The air used for analysis was synthetic air obtained from Hoek Loos (21% O_2).

EXPERIMENTAL RESULTS AND DISCUSSION

During introductory (batch) experiments using a stirred cell with an undisturbed, flat gas–liquid interface, the formed copper sulfide particles floated on the liquid surface, probably due to their hydrophobic nature. This hampered the interpretation of the experimental results. Therefore, the mechanically agitated gas–liquid reactor (in which the gas–liquid interface is less static) was subsequently chosen as a model reactor. An extra advantage of the MAGLR is that the gas–liquid behaviour of a MAGLR more closely resembles that of an industrial absorber than that of a flat interface model reactor. A drawback of this reactor type appeared to be that the residence time distribution (RTD) of the gas phase could not be

[3]At a temperature of 273 K and a pressure of 1.013 bar.

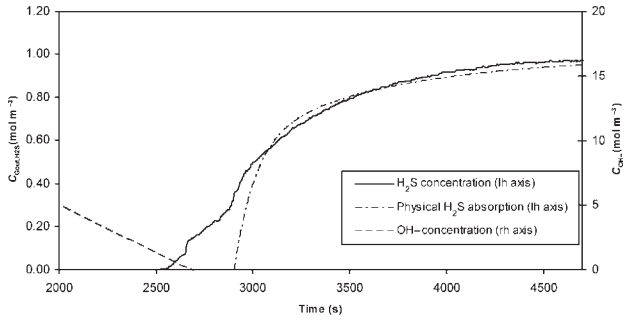

Figure 3. The concentration of H_2S in the gas stream leaving the reactor, and the concentration of NaOH as a function of time. $T = 293$ K, $P = 120\ 000$ Pa, $V_L = 600$ ml, $\Phi_G = 5$ Nml s^{-1}, $N = 200$ rpm, $H_2S = 2$ V%, $NaOH_{init} = 0.0198$ M. As reference the theoretical H_2S concentration that would occur at the outlet in the case of physical absorption in a non-reactive liquid is also shown.

described by plug flow nor by CISTR[4] like behaviour. A review article by Joshi *et al.* (1982) concludes that the gas phase RTD in MAGLRs is equivalent to a single CISTR or two CISTRs in series or in between the two. Hanhart *et al.* (1963) found that the RTD of the gas phase can be described adequately by a single CISTR at stirring speeds above the critical stirring speed[5] (900 rpm for the setup used). At lower stirring speeds, as mostly applied during this study, the RTD of the gas phase can be described by two CISTRs in series. Thus, the concentration of the gas leaving the reactor is not representative for the concentration of the gas phase in the reactor. This is especially important when the H_2S conversion is high, and H_2S concentrations in the gas phase may vary considerably from bubble to bubble.

Absorption of H_2S in NaOH Solutions

To characterize the experimental setup, an H_2S absorption experiment using an aqueous 0.0198 molar NaOH solution was performed. This experiment was continued up to the point where the NaOH solution was fully depleted. The reaction between H_2S and NaOH is known to be instantaneous with respect to mass transfer (Danckwerts, 1970). The H_2S absorption in a NaOH solution is therefore usually gas phase mass transfer limited, provided the gas does not consist of pure H_2S and the concentration of NaOH is sufficiently high. Therefore this experiment was suitable to determine the H_2S concentration in the gas leaving the reactor in the case of a gas phase limited mass transport process. At the start of the experiment 600 ml of a NaOH solution was added to the reactor. After the desired reaction temperature was reached a gas stream containing 2 V% H_2S was fed to the reactor. In steady state (up to t = 2000 s) the concentration of H_2S in the gas leaving the reactor varied around 30 ppmV. The result of this experiment is shown in Figure 3. The NaOH concentration in the reactor was estimated by integration over the H_2S mass balance in time. It appeared that the H_2S concentration of the gas leaving the reactor was not a function of the NaOH concentration of the solution until the NaOH solution was nearly depleted. Thus, up to this point H_2S absorption apparently takes place in the gas phase mass transfer limited regime as was also expected [see also equation (15)]. When the solution is depleted the H_2S concentration in the reactor effluent increases rapidly. As reference the theoretical H_2S concentration that would occur at the outlet in the case of physical absorption in a non-reactive liquid is also shown. The time at which the theoretical curve for the physical H_2S absorption starts was chosen arbitrarily but, of course, after the experimental time at which H_2S breakthrough occurred ($\sim$2500 s). As can be seen in Figure 3, there is a remarkable resemblance between the two curves, especially from $C_{H_2S,G,out}/C_{H_2S,G,in} > 0.4$.

Absorption of H_2S in $CuSO_4$ Solutions

With the physical characteristics of the reactor known, the absorption of H_2S in a copper sulphate solution was studied using a copper sulphate solution. An introduction experiment was carried out using a 0.5 M $CuSO_4$ solution. For H_2S concentrations of 4% or more foaming occurred (this effect was also mentioned in Ter Maat *et al.*, 2005). Therefore, the H_2S concentration in the feed gas was kept at 2%. It appeared that before break through of H_2S ($<$12000 s) very high H_2S conversions could be obtained for a H_2S percentage in the feed gas of 2 V% or lower; concentrations of H_2S in the reactor effluent varied between 20 and 40 ppmV, which is comparable to the H_2S concentration when using a NaOH solution as absorbent.

Next, an experiment was carried out with 0.1 M $CuSO_4$ solution up to the point where the $CuSO_4$ solution was fully depleted. As with the NaOH absorption experiment the concentration of H_2S in the gas leaving the reactor in steady state (up to $t \sim 13\ 000$ s) again varied around 30 ppmV. The $CuSO_4$ concentration had no influence on the H_2S conversion until the $CuSO_4$ concentration dropped below a very low 4–10 mol m^{-3}, see also Figure 4 (the copper concentration in the liquid was estimated from the integration of the H_2S mass balance, the accuracy of this mass balance was approximately 5–10%). Only after the $CuSO_4$ concentration dropped below 4–10 mol m^{-3}, indicating a Cu^{2+} conversion of more than 90%, the H_2S concentration in the reactor effluent started to increase. Taken together with the results from the NaOH experiments this demonstrates that the H_2S absorption in a copper sulphate solution most

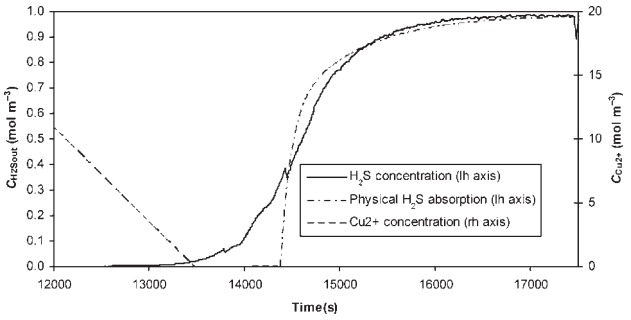

Figure 4. The concentration of Cu^{2+} in the liquid and the concentration of H_2S in the gas stream leaving the reactor as a function of time. $T = 293$ K, $P = 120\ 000$ Pa, $V_L = 700$ ml, $\Phi_G = 5$ Nml s^{-1}, $N = 200$ rpm, $H_2S = 2$ V%, $CuSO_{4,init} = 0.1$ M. As reference the theoretical H_2S concentration that would occur at the outlet in the case of physical absorption in a non-reactive liquid is also shown.

[4]Continuously ideal stirred tank reactor.

[5]The critical stirring speed is defined as the stirrer speed at which the k_La is notably influenced by the stirrer speed.

Table 2. The concentration of H_2S in the gas stream leaving the reactor as a function of stirrer speed. $T = 293$ K, $P = 120\,000$ Pa, $V = 700$ ml, $N = 200$ rpm, $H_2S = 2$ V%, $CuSO_4 = 0.1$ M.

N (rpm)	H_2S (ppmV)
50	39.0
100	45.3
150	35.1
200	33.2
250	42.2

probably takes place in the gas phase mass transfer limited absorption regime if the copper concentration is sufficiently high. Because of this, a reliable performance of copper sulphate based industrial gas desulphurization units can be assured as long as there is a low concentration of copper ions in the solution. When the solution is completely depleted of Cu^{2+}, the H_2S concentration in the reactor effluent increases rapidly. As reference the increase in H_2S concentration that would occur in the case of physical absorption only is also shown in Figure 4. Just as in the case with NaOH, the experimental breakthrough curve has a close resemblance to the theoretically calculated physical breakthrough curve.

In a series of experiments the influence of the stirrer speed on the H_2S concentration in the reactor effluent was investigated using a 0.1 M $CuSO_4$ solution as absorbent (see Table 2). Within the experimental accuracy, the concentration of H_2S in the reactor effluent did not depend on stirrer speed. This can be explained since the relatively small increase in the overall gas phase mass transfer coefficient that occurs with increasing stirrer speed may be offset by the increasing fraction of gas bubbles with a relatively short residence time (the gas phase will show a more CISTR-like behavior with increasing stirrer speed).

DISCUSSION

Comparison Model and Experimental Results

H_2S absorption experiments were carried out using an H_2S concentration of 2 V% and a copper concentration that varied between 0.01 and 0.1 mole dm^{-3}. The removal of H_2S took place very efficiently. The experimental results show that the concentration of H_2S in the gas leaving the reactor is comparable to the concentration of H_2S in the gas leaving the reactor in case of a gas and liquid phase mass transfer limited absorption process (30–60 ppm and 60 ppm resp.).

As can be seen in Figures 5–7, results from the models show that, for a H_2S concentration of 2 V% and a copper concentration of approximately 0.1 mole dm^{-3} (the conditions at which the experiments where carried out) a significant difference between the H_2S absorption rate predicted by the extended model (incorporating mass transfer and crystal growth kinetics) and the simplified model (assuming a mass transfer limited process) exists. The results of the simplified model are in accordance with the observations that can be made from the experiments, while the results from the extended model deviate from these observations.

Hence in can be concluded that the experiments have shown that the applicability of the simplified model description is better than the extended model for the experimental

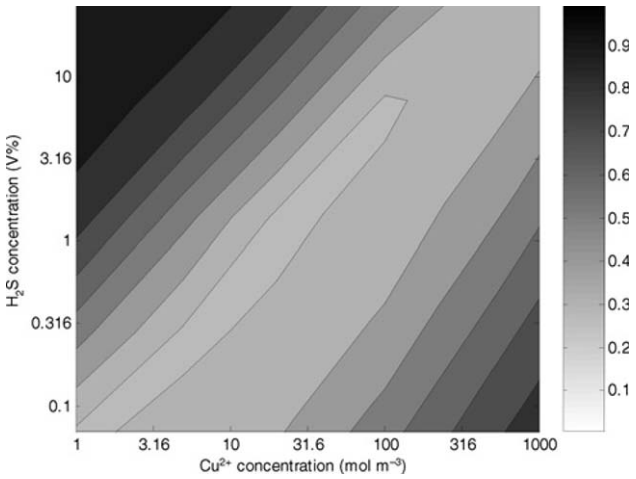

Figure 5. Absorption of H_2S in a $CuSO_4$ solution: ratio of simulated absorption rate according to the extended model and the absorption rate according to the simplified model at pH = 5.5, $k_L = 1.1 \times 10^{-5}$ m s^{-1}, $k_G = 1.1 \times 10^{-4}$ m s^{-1}.

conditions applied and that the extended model gives, for the experimental conditions applied, an under prediction of the H_2S absorption rate. This can be explained since, for the extended model, the kinetic parameters (particle birth and growth) are fitted from the particle size distribution of the produced CuS, and not fitted taking the H_2S absorption rate into account. Hence the extended model will be more aimed at giving a correct prediction of the particle size distribution of the produced CuS, than at giving a correct prediction of the H_2S absorption rate.

Also bear in mind that, biogas contains (usually) less than 2 V% H_2S, while the preferred concentration of $CuSO_4$ in a $CuSO_4$ based desulphurization unit will be more than 200 mol m^{-3} (Ter Maat *et al.*, 2005). Hence the conditions under which an actual desulphurization unit will operate are such that the removal of H_2S from biogas can be efficient and will therefore probably take place in the gas phase mass transfer limited regime.

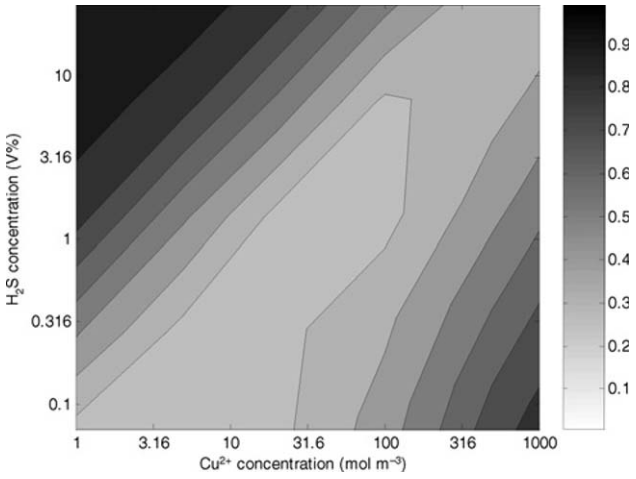

Figure 6. Absorption of H_2S in a $CuSO_4$ solution: ratio of simulated absorption rate according to the extended model and the absorption rate according to the simplified model at pH = 3.5, $k_L = 1.1 \times 10^{-5}$ m s^{-1}, $k_G = 1.1 \times 10^{-4}$ m s^{-1}.

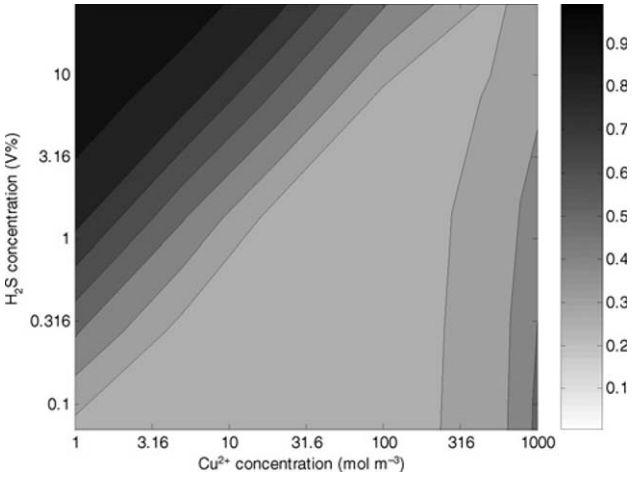

Figure 7. Absorption of H_2S in a $CuSO_4$ solution: ratio of simulated absorption rate according to the extended model and the absorption rate according to the simplified model at pH = 2.0, $k_L = 1.1 \times 10^{-5}$ m s^{-1}, $k_G = 1.1 \times 10^{-4}$ m s^{-1}.

Comparison Simplified and Extended Model Results

As already pointed out in the section 'Mass transfer models', if the precipitation reaction is sufficiently fast, the absorption of H_2S in the Me^{2+}-ions containing solution may be regarded as absorption of a gaseous component into a solution, accompanied by a very fast irreversible reaction. This can occur when the driving force for the precipitation reaction is sufficiently high (as is usually the case for the formation of highly insoluble metal sulphides). In this case the absorption rate can be described with equation (15) or, in the case of gas phase mass transfer limitation equation (17), which can be regarded as limiting cases of the extended model given by Al-Tarazi *et al.* (2004). This simplification allows for a considerable reduction in modeling effort and the (computation) time needed for the design of a gas–liquid contacting device. Of course, this simplified approach will not allow for the calculation of the particle size distribution of the precipitate.

The ratio of the absorption rate as obtained with the extended model by Al-Tarazi to the flux predicted by the simplified model [Equations (13) and (15)] is shown in Figures 5–7. Each plot shows the ratio at a different pH. The ratio varies from 0.3 to 0.4 (lighter grey area) to 1.0 (black).

From these figures it can be seen that the differences between the flux as predicted by the simplified model and the predicted flux according to the extended model decreases with increasing pH. This is a consequence of the fact that the reaction rate between H_2S and Cu^{2+} predicted by the extended model decreases with decreasing pH.

Furthermore, it can be seen that the differences between the maximal possible flux as predicted by the simplified model and the predicted flux according to the extended model are relatively small (<30%) for large areas of the investigated combinations of Cu^{2+} and H_2S concentrations. At high concentrations of H_2S and low concentrations of Cu^{2+} the differences are negligible. Under process conditions that could realistically occur in a biogas desulfurization unit (<2% H_2S, high copper concentration, pH 3.5 or higher), the simplification can also be applied, however loss of accuracy (differences 30–45%) will occur.

At the remaining, more extreme, combinations Cu^{2+} and H_2S concentrations the simplified model will give a significantly different result than the extended model (the lighter areas in Figures 5–7, indicating differences up to 60%).

CONCLUSIONS

In this study the desulphurization of gas streams using aqueous copper sulphate ($CuSO_4$) solutions as washing liquor has been studied theoretically and experimentally.

Absorption experiments were carried out in a Mechanically Agitated Gas Liquid Reactor. This reactor was characterized using the absorption of CO_2 in water. The results matched reasonably well with relations found in literature (in the area that those relations are valid). H_2S absorption experiments were conducted at a temperature of 293 K and $CuSO_4$ concentrations between 0.01 and 0.1 M. These experiments showed that the copper sulfate solution efficiently removes H_2S even at very low copper concentrations. The experimental results indicate that for industrially relevant process conditions the absorption of H_2S in a $CuSO_4$ solution may be considered a gas phase mass transfer limited process. This will result in a reliable performance of copper sulphate based industrial gas desulphurization units.

An extended model developed by Al-Tarazi *et al.* (2004) has been used to predict the rate of H_2S absorption and results of it were compared to the results obtained with a simplified mass transfer model that assumes an instantaneous irreversible reaction. This comparison showed that for many industrially relevant conditions the simplified model is able to predict the absorption rate of H_2S in a $CuSO_4$ solution within 30% of the exact result of the extended model. Under a much wider range of conditions the error the results of the simplified model are still within engineering accuracy of the theoretical result of the extended model.

Furthermore it was shown that the results from the simplified model correspond with the experimental results, while a difference between the H_2S absorption rate predicted by the extended model and the experimental results exists. For the experimental conditions applied the extended model gives a prediction for the H_2S absorption rate that is lower than the absorption rate indicated by the experiments. This deviation may be caused by that the fact that extended model was set up as a description of the precipitation process, rather than being set up to give an accurate description of the absorption rate.

NOMENCLATURE

a	specific surface area, m^{-1}
g	exponent in growth rate expression
k	reaction constant, s^{-1}, m^3 mole^{-1} s^{-1}
k	mass transfer coefficient, m s^{-1}
m	gas distribution coefficient
n	exponent in nucleation rate expression
r	reaction rate, mole m^{-3} s^{-1}
t	time variable, s
x	place variable, m
z	ion valence
A	area, m^2
B	particle nucleation rate, mole m^{-3} s^{-1}
C	concentration, mole m^{-3}
D	diffusion coefficient, m^2 s^{-1}
E	residence time distribution
E	chemical enhancement factor
F	Faraday constant, C mole^{-1}

G	particle growth rate, m s^{-1} or mole m^{-3} s^{-1}
J	gas absorption rate, mole m^{-2} s^{-1}
K	equilibrium constant, mole m^{-3}
L	particle diameter, m
N	stirrer speed, rpm
R	universal gas constant, J $mole^{-1}$ K^{-1}
S	degree of supersaturation
T	temperature, K

Greek Symbols

α	particle volume to length factor, m^2
β	particle surface to length factor, m
ϕ	electrostatic potential gradient, V m^{-1}
γ^s	surface tension, J m^2
ρ	density, kg m^{-3}
Δ	denoting a difference

Subscripts

a	referring to acidity
g	referring to particle growth
i	referring to component *i*
n	referring to particle nucleation
w	referring to water
G	referring to gas
L	referring to liquid
OV	overall
SP	referring to the solubility product
0	referring to critical nucleus
∞	infinite

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